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13. ABSTRACT *(Maximum 200 words)*

The research on the fracture and fatigue crack-growth behavior of single crystal intermetallics was motivated by the need for improved high temperature engineering materials. The approach using a first principles total energy calculation of the energies of {001} and {110} surfaces in NiAl, by Yoo and Fu predicts very low fracture toughness vs. experimental findings. As the program has developed, the focus has shifted to the use of thermal barrier and wears resistant coatings to improve material behavior at high temperature and other extreme service conditions. The present emphasis therefore to develop thermal barrier and wear resistant coating systems with improved integrity and long term reliability. The major accomplishment of this work has been the development of fracture-mechanics based techniques to accurately and reproducibly measure the fracture resistance (or adhesion) of coating systems. We believe the data presented to be unique for the two coating systems characterized. Interface toughness, K , data was obtained for several specimens containing multi-layer systems of PSZ-NiAl-Pt- Superalloy and TiAlN-Cermet. The interfaces prone to fracture were identified. Experiments were also completed to analyze crack-growth under cyclic fatigue loading of these interfaces.

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Fracture and Fatigue Crack-Growth Behavior of Interfaces in Thermal Barrier and Wear Resistant Coating Systems

Submitted to:

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September 1998

Fracture and Fatigue Crack-Growth Behavior of Interfaces in Thermal Barrier and Wear Resistant Coating Systems

Objectives

The objective of our final year of the AASERT program has been to develop thermal barrier and wear resistant coating systems with improved integrity and long term reliability. A fundamental understanding of fracture and fatigue debond-growth behavior at or near the interfaces formed between these multi-layer coating systems and their substrates is necessary to tailor processing parameters to achieve optimal performance. The use of novel materials for the bond coat layer (NiAl+Pt) and the coating (PSZ) makes this effort more challenging, as little engineering data exists for these materials in either bulk form or as thin layers.

Status of Effort

1. Introduction

Although thermal barrier coatings (TBC's) have been used in stationary components of turbines for over three decades, their application to rotating turbine blades and vanes in the hotter section of engines is more recent. The principal way of increasing turbine efficiency is to increase inlet temperatures. In order to use TBC's in such dynamic, high temperature, and corrosive environments, a fundamental understanding of the fracture (adhesion) and fatigue (progressive debonding) modes is essential. The intent of the present year's effort has been to explore these issues in a zirconia (TZP) thermal barrier coating system as well as a TiAlN hard coating. The work forms part of a broader effort included in our parent AFOSR program that will be reported separately.

The thermal barrier system consisting of the TZP coating on a single crystal superalloy substrate with a NiAl-Pt bond layer represents the state-of-the-art in high temperature corrosion and oxidation protection for structural parts in advanced turbine engine systems. Zirconia possesses excellent thermal shock resistance, low thermal conductivity, and relatively high coefficient of thermal expansion. The hard coating system consists of a TiAlN coating on a cermet substrate which is used extensively in the cutting tool industry. First introduced in the 1960's, hard coatings were incorporated into cutting tool systems primarily to provide wear resistance. As in the case with turbine blades, these coatings allow increased speeds, thus optimizing system efficiency.

Decohesion of the coating systems usually occurs at or near the coating–bond coat interface. The objective of the AASERT program has been to develop fracture mechanics based testing methods to assess the critical adhesion values of these interfaces. Despite their importance, little quantitative data currently exists for these interface systems. Using fracture mechanics concepts, the driving force for the extension of an interface crack or debond can be expressed by the strain energy release rate, $\mathcal{G}_i$.

In the present work, we have developed a novel bonding technique to sandwich the coating system of interest between two similar elastic substrates and then use standard double-cantilever fracture mechanics samples (DCB) to measure the interface fracture resistance. The DCB specimen is an attractive test geometry, both from an experimental and theoretical mechanics point of view. A pre-notch is introduced in the sample by machining or during sample preparation. As load is applied, a crack initiates ahead of the notch and deflects to the weaker interface in the sandwich structure.

2. Results

Thermal Barrier Coatings:

Results of our investigations of the adhesion and debonding of TBC's on super alloy substrates were described in last years progress report.

Wear Resistant Coatings:

DCB samples containing the wear resistant coating systems were initially loaded under fatigue loading conditions. A crack initiated from the weak region of the interface and dived into the interface between the hard coating and the cermet substrate. Following such pre-cracking, the debond could be grown in a relatively stable fashion under monotonic loads using displacement control.

Critical interface adhesion values were obtained using similar methods described for the TBC samples. An average critical fracture toughness value of 3.14 $MPam^{1/2}$ (S.D. = 0.14 $MPam^{1/2}$) was determined. Using a compliance technique, fracture toughness values could also be obtained during stable debond extension. The average fracture toughness value obtained was 3.4 $MPam^{1/2}$ with a S.D. of 0.144 $MPam^{1/2}$.

A more complete description of the work, together with a determination of the weak layer in the multi-layer coating system and full microstructural analysis of the region surrounding the fracture interface is described in the attached publication.

Accomplishments/New Findings

The major accomplishment of this work has been the development of fracture-mechanics based techniques to accurately and reproducibly measure the fracture resistance (or adhesion) of coating systems. We believe the data presented to be unique for the two coating systems characterized. Interface toughness, K_c, data was obtained for several specimens containing multi-layer systems of PSZ-NiAl-Pt-Superalloy and TiAlN-Cermet. The interfaces prone to fracture were identified. Experiments were also completed to analyze crack-growth under cyclic fatigue loading of these interfaces.

Personnel Supported

Graduate Students: Joanna Mroz (graduated June 1998, M.Sc.)

Publications

J. Mroz, R. H. Dauskardt and U. Schleinkofer, "New Adhesion Measurement Technique for Coated Cutting Tool Materials," International Journal of Refractory Metals and Hard Materials, 1998. In press.

Interactions

Research was undertaken in collaboration with Dr. M. L. Jackson at the G. E. Corporate Research and Development Center, and Dr. U. Schleinkoffer of Kennemetal, both of whom supplied materials for the study. Data produced in the program was useful to the thermal barrier program at G. E. and the hard materials coating program at Kennemetal.

Consultative Functions
None

Transitions
None

New Discoveries
None

Honors/Awards

Awards Received in 1996/97
None

Major Awards Received Prior to 1997/98

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1978 Fellow, ASM, Metals Park, OH.
1979 Champion Herbert Mathewson Gold Medal, American Institute for Mining, Metallurgical and Petroleum Engineers
1987 Elected to National Academy of Engineering
1988 Institute of Metals Lecturer and Robert Franklin Mehl Medalist, TMS (AIME)
1988 Elected Fellow of TMS (AIME)
1989 Edward DeMille Cambell Memorial Lecturer, ASM
1993 Acta Metallurgica Gold Medal
1995 Educator Award of The Minerals, Metals & Materials Society (TMS)

Reinhold H. Dauskardt

1989 U.S. Department of Energy, Most outstanding Scientific Accomplishment Award.
1995 Dana Griffen Award for Innovative Research from Stanford University.

New Adhesion Measurement Technique for Coated Cutting Tool Materials

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In press.

Abstract

Adhesion properties of wear resistant coatings on cutting tool materials are essential to their performance in technical applications. It is therefore necessary to characterize the coating adhesion by an appropriate measurement technique which reveals both critical adhesion values as well as information on time dependent debonding. In particular, a quantitative and reproducible technique is required rather than largely qualitative methods such as indent or scratch tests. In addition, for multilayer coatings, the location of the weakest interface is required to facilitate improvement of interfacial integrity.

Accordingly a sandwich double cantilever beam (DCB) test was developed and used to measure the adhesion properties of coatings on cermets. Additionally, the structure of the coatings in the as fabricated state and after mechanical testing were characterized by optical microscopy, SEM, and TEM. With quantitative adhesion measurements and investigations of the interface microstructure, a comprehensive characterization of coating adhesion on cutting tool materials was achieved.

1) Introduction

One important development in the performance of cemented carbides was the introduction of wear resistant coatings like TiC, TiN, Ti(C,N), Al_2O_3, TiAlN, and diamond **/1/**. Two different techniques are typically used to deposit these coatings as a single, thick layer or as multilayer systems: physical vapor deposition (PVD) and chemical vapor deposition (CVD). Recent developments successfully used both techniques in one multilayer system (PVD TiN on top of a CVD TiN/Ti(C,N) layer) which showed significantly improved performance **/2/**.

The adhesion properties of coatings on cemented carbide substrate materials are essential to their performance during cutting processes and wear applications. It is therefore necessary to characterize the bond strength

between different coating layers and between the coating structure and the substrate by appropriate measurement techniques. Ideally, these should reveal both critical adhesion values as well as information on time dependent debonding. In particular, a quantitative, reproducible, and reliable technique is required. Existing methods such as indent or scratch adhesion tests as well as several variations of pull-off tests which are commonly used in industry, provide principally qualitative results for quality management and development of new coating systems **/3,4/**. An additional complication with these techniques is that relaxation of residual stresses in the coatings that occurs during testing may significantly affect the measured adhesion values. Finally, for multilayer coatings, which are frequently used in cutting tool applications, the location of the weakest interface is required to facilitate improvement of interfacial integrity.

Accordingly, the intent of the present study was to develop a mechanical adhesion technique based on controlled debonding in a fracture mechanics sample. This technique is based on similar methods recently developed to measure adhesion in thin film structures found in microelectronic devices **/5-9/**. Such techniques combined with an investigation of the microstructure facilitate a better understanding of bonding mechanisms of ceramic coatings

on cemented carbides. Data obtained is compared to existing, qualitative scratch test techniques.

2) **Experimental Methods**

2.1) Material

A Ti(C,N)-based cermet with a 3-4μm thick PVD TiAlN coating was selected for study. Adhesion values were determined for different pre-coating surface preparation methods. Two different techniques were used to change the surface morphology of the substrate material: sandblasting and additional microblasting. Typical sandblast media were AlN, Al_2O_3 or glass particles with particle sizes around 500μm; microblast media were Al_2O_3 particles with particle sizes around 10μm. The surface morphologies obtained are shown in **Fig. 1** and were measured using a WYKO non-contact optical profiler system. Surfaces were also characterized by SEM. Roughness data obtained is presented in **Table 1** together with definitions of roughness parameters employed. There was no significant change of the roughness parameters R_z and R_t for the sandblasted, and sandblasted and microblasted samples. However, R_a and R_q values indicate a smoother surface after microblasting.

Weight measurements were conducted before and after the surface treatment to calculate the amount of material removed during the sandblast and

microblast processes. 4μm of material was removed during the sandblasting treatment compared to only 0.2μm for the microblasting treatment. Conventional practice was used to deposit a 3-4μm PVD TiAlN coating.

2.2) Adhesion Measurement

The fracture mechanics based tests were conducted on DCB specimen in which the hard coating was sandwiched between two cermet substrates (**Fig.2**). To achieve a satisfactory bonding between the coating and the additional substrate surface an Ag-Cu-alloy was employed using a vacuum brazing technique. The bonding temperature was 800°C. **Fig. 3** shows a 20μm bonding layer between a PVD-TiAlN coated and an uncoated substrate material which was bonded to test the strength of different bonding procedures. A 5 mm region with no braze serves as a blunt notch for debond initiation between the substrate and the PVD-coating during testing. Crack path analysis was performed during and after the experiment by optical microscopy and SEM to verify the debonding of the coating from the substrate.

A micro-mechanical test system capable of applying very accurate small displacements (15 nm) was employed using a piezoelectric actuator and high stiffness load cells (**Fig. 4**). The debond length was measured in-situ using an

optical microscope and was also calculated using compliance techniques. Load-displacement data was monitored and recorded on an X-Y plotter. Peak values of load (on a load-displacement graph) prior to incipient debond extension were used to determine the critical interface fracture energy, G_C. One of the benefits of employing the sandwich DCB is the constraint of residual stresses during debonding. In this geometry, the massive substrates (compared with the thin film coating) restrain any relaxation of residual stresses in the coating.

Adhesion values are determined using a fracture mechanics methodology. The debond driving force, expressed in terms of the strain energy release rate, G, is a function of the loading configuration and elastic properties. The interface fracture energy, $G_c(\psi)$ is dependent on the phase angle of loading, ψ, which represents the ratio of shear (Mode II) to normal (Mode I) stresses acting near the crack tip. These considerations are not addressed further in the present study but are required for a more complete understanding **/10/**.

Debond extension occurs when:

$$G_i \geq G_c(\psi)$$

From known load and displacement data, a G_C can be determined using the following standard fracture mechanics based solution:

$$G_c = 12 * \frac{P^2 a^2}{E' b^2 h^3} (1 + .64 \frac{h}{a})^2$$

where P is the load, a is the debond length, E is Young's Modulus, b is the sample width and h is the half-thickness of the specimen.

From load-displacement data debond lengths (in addition to those measured optically) may be calculated using the following compliance relationship:

$$Compliance = \frac{\delta}{P} = \frac{4a^3}{Ebh^3}\left[1 + 1.92\frac{h}{a} + 1.22\frac{h^2}{a^2} + .39\frac{h^3}{a^3}\right]$$

where δ is the displacement, and P is the load. The room temperature adhesion of the coatings was tested by both the traditional scratch test technique and the new sandwich DCB test.

2.3) Microstructure

Samples were prepared for optical microscopy, SEM, and TEM investigations to determine the microstructure of the substrate and coating. In addition, cross sectional sample preparation techniques were used to characterize the microstructure close to the interface between the substrate and coating, both before and after adhesion testing. For the preparation of specimen sites near the coating to substrate transition, an ion beam thinning apparatus (GATAN – Precision Ion Polishing System) was used.

3) Results and Discussion

3.1) Adhesion Measurement

The interface fracture energy for the two different substrate preparation techniques was measured and data is presented in **Fig.5**. The adhesion data obtained using optical and compliance measurements of the debond length resulted in very similar values. **(Table 2)** The system receiving the sandblast treatment had an average fracture energy of 4.3 J/m^2. Sandblasting followed by microblasting significantly increased the adhesion at the interface to an average of 27.8 J/m^2, over six times the adhesion of the sandblast system. The measured data was in agreement with similar trends observed using the scratch test. From these experiments, the sandblasted samples showed a significantly reduced critical load compared to the sample with additional microblasting treatments (**Fig.6**).

It should be noted, however, that the fracture energy data obtained may by influenced by the brazing temperature employed during the bonding process. While the brazing time is short, limited diffusion of the braze material into grain boundaries of the coating during bonding may result in increased adhesion values. Similar diffusion bonding techniques employed to measure adhesion of TiN/SiO_2 interfaces in microelectronic interconnects showed no significant effects of the high temperature bonding step **/5,6/**. In the present

study, no significant microstructural effects of the elevated temperature brazing was noted in the TEM investigation. Indeed, for the short brazing times and relatively low temperatures involved, only very limited diffusional changes are anticipated for the present refractory materials. However, more indepth studies are required to elucidate any changes associated with diffusional processes.

In general, during debond growth, two energy dissipation processes contribute to the macroscopic adhesion energy. The first of these processes is associated with the near tip fracture process and includes energy associated with breaking chemical bonds across the interface. The second process occurs when energy is dissipated behind the debond tip from debond face interactions, such as frictional sliding of contacting asperities **/5-9/**. Increases in adhesion are typically observed if the roughness of the interface is increased **/9/**. The microstructural basis for the difference in adhesion energy measured for the present coating systems is discussed in the following section.

3.2) Microstructure

Fig.7 shows a combination of a polished optical cross section, a TEM micrograph of the substrate, and SEM fracture cross section of a coated sample. The coating thickness was found to be 3-4μm with a typical columnar

structure visible in the SEM fracture cross section. TEM investigation of the cermet showed a fine grain microstructure with grain size of the ceramic phase particles of about 1μm.

For both the sandblasted and sandblasted + microblasted samples, the optical crack path analysis showed that the debond path is located at the interface between the TiAlN coating and the cermet substrate (**Fig.8**). This indicates that the interface between the substrate and PVD-coating is the weak microstructural path in the layered system. SEM and TEM cross section micrographs are shown in **Fig.9** for the sandblast surface condition, which showed a significantly lower adhesion value. In TEM cross section, where transparent regions of the coating and substrate were obtained, a layer of cracked ceramic particles parallel to the surface was found close to the substrate interface. This damaged layer was determined to be ~1μm thick and most probably caused by the sandblasting. Microblasting removes the damaged layer thereby allowing the coating to bond to the undamaged substrate. The reduced adhesion energy of the sandblast samples therefore appears to be caused by a reduced fracture energy of the substrate material directly under the coating. This suggests that changes in the energy dissipation in the near-tip fracture process zone (rather than differences in the

wake dissipation zone associated with interface roughness) contribute to the difference in adhesion energy between the two substrates preparations.

4) Conclusions

(a) A novel measurement method was developed which provides quantitative adhesion values for hard coatings on cutting tool cermet substrates. Consistent adhesion data was obtained from independent optical and compliance techniques used to measure the debond length. Results exhibit the same trends as those obtained from the traditional scratch test technique.

(b) Substrate surface processing conditions significantly affect interface adhesion values of the wear resistant coatings on cermet substrates.

(c) The crack path appears to be at the coating to substrate interface or immediately below in the substrate material.

(d) Cross section TEM on the sandblasted samples showed a damaged layer in the substrate material, which is responsible for reduced adhesion values.

Acknowledgments

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/10/ J. Hutchinson, Z. Suo. Advances in Applied Mechanics, 63-191, 1991.

Table 1: Roughness data measured for a sandblasted and an additionally microblasted cermet substrate.

Roughness parameter	Sandblast	Sandblast + Microblast
R_a	573.01	521.28
R_q	729.77	667.74
R_z	6.99	6.93
R_t	7.51	8.15

R_a: average roughness (nm)

R_q: root mean square roughness (nm)

R_z: average maximum height of profile (nm)

R_t: maximum height of profile (nm)

Table 2: Average critical interface fracture energy for the sandblast and sandblast/microblast surface preparation techniques.

Fracture Energy, G_c (J/m^2)		
	Sandblast	Sandblast/Mircoblast
Debond Measurement Technique		
Optical	4.19	24.74
Compliance	4.34	29.74
Average	4.29	27.78

Figure captions

Fig. 1: Surface morphologies measured using a WYKO non-contact optical profiler system and SEM characterization of a sandblast and a sandblast + microblast cermet substrate material (see Tab.1 for results).

Fig. 2: Schematic illustration of the DCB specimen showing thin (4μm) ceramic coating sandwiched between two thick cermet substrates.

Fig. 3: Optical micrograph of the developed bonding layer between cermet substrate material and a PVD-TiAlN coating.

Fig. 4: Schematic illustration of micro-mechanical testing system used to measure adhesion.

Fig. 5: Interface fracture energy plotted as a function of debond length for both surface preparation techniques.

Fig. 6: Scratch test results for both sandblast and sandblast + microblast substrate processing conditions.

Fig. 7: Optical micrograph of polished cross section, TEM micrograph of substrate material, and SEM micrograph of fracture cross section of TiAlN PVD coated cermet.

Fig. 8: Optical micrograph showing cross-section of the TiAlN coating and cermet substrate. Debond path appears to be at the coating to substrate interface.

Fig. 9: SEM micrograph of fracture cross section and TEM micrograph of TiAlN PVD coated cermet in cross section in sandblasted surface condition.

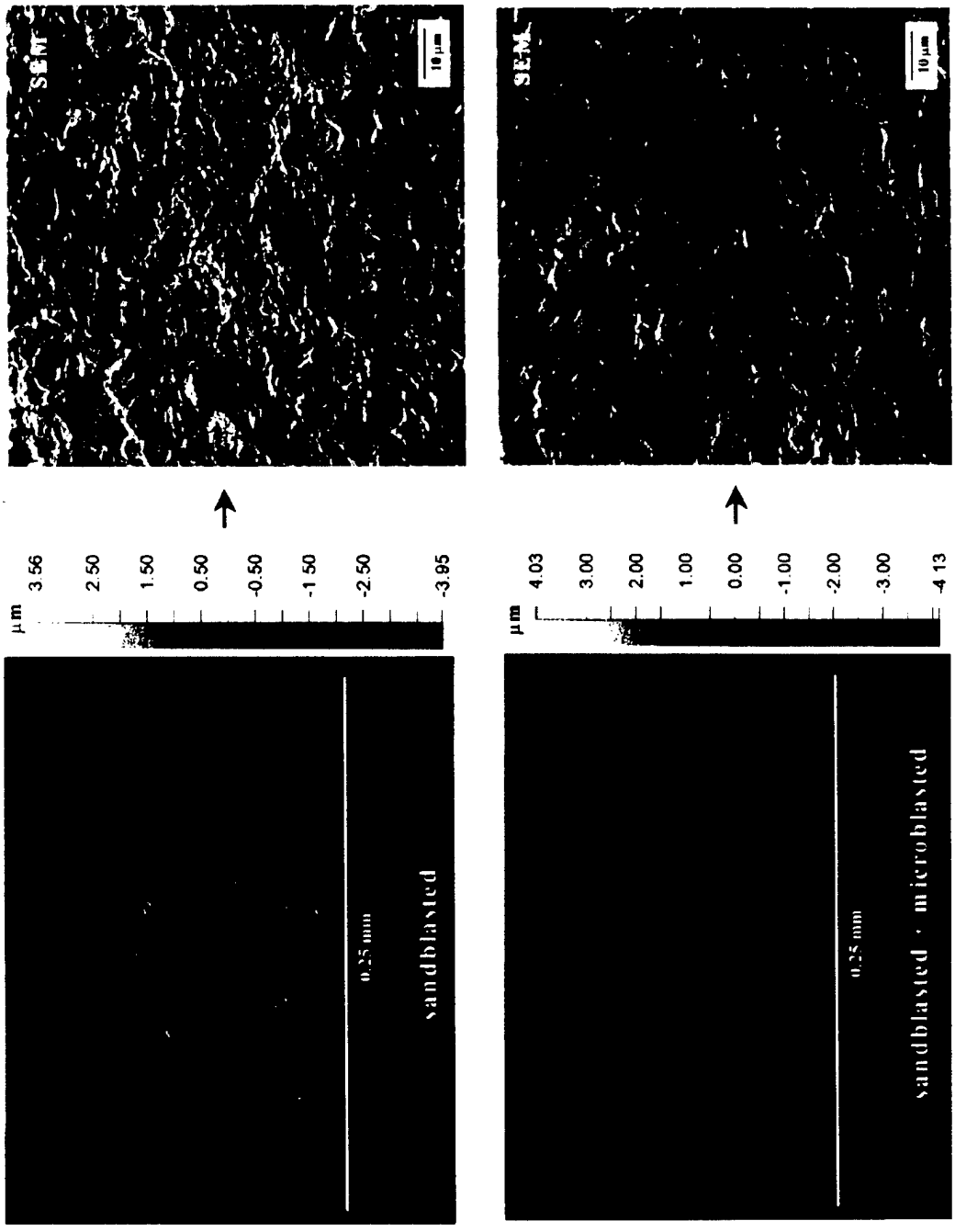
SEM
10 µm
µm
3.56
2.50
1.50
0.50
-0.50
-1.50
-2.50
-3.95
0.25 mm
sandblasted
SEM
10 µm
µm
4.03
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
-4.13
0.25 mm
sandblasted + microblasted

Fig.1

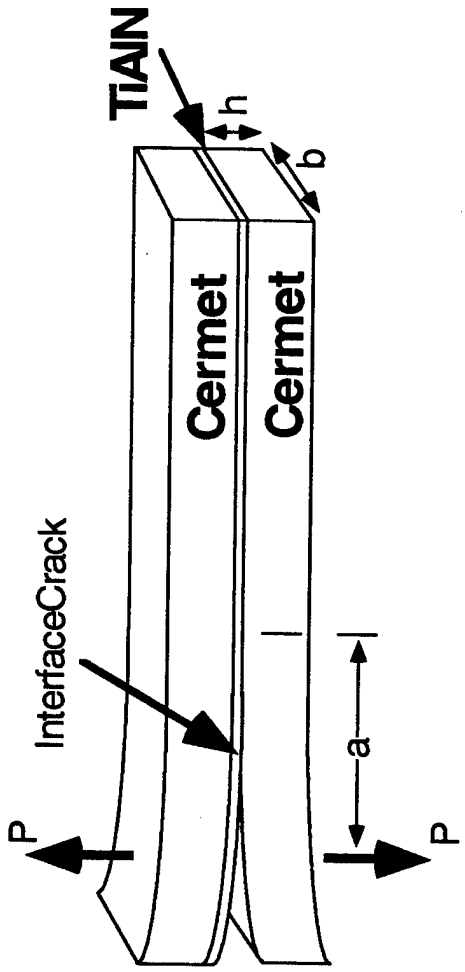

Fig.2

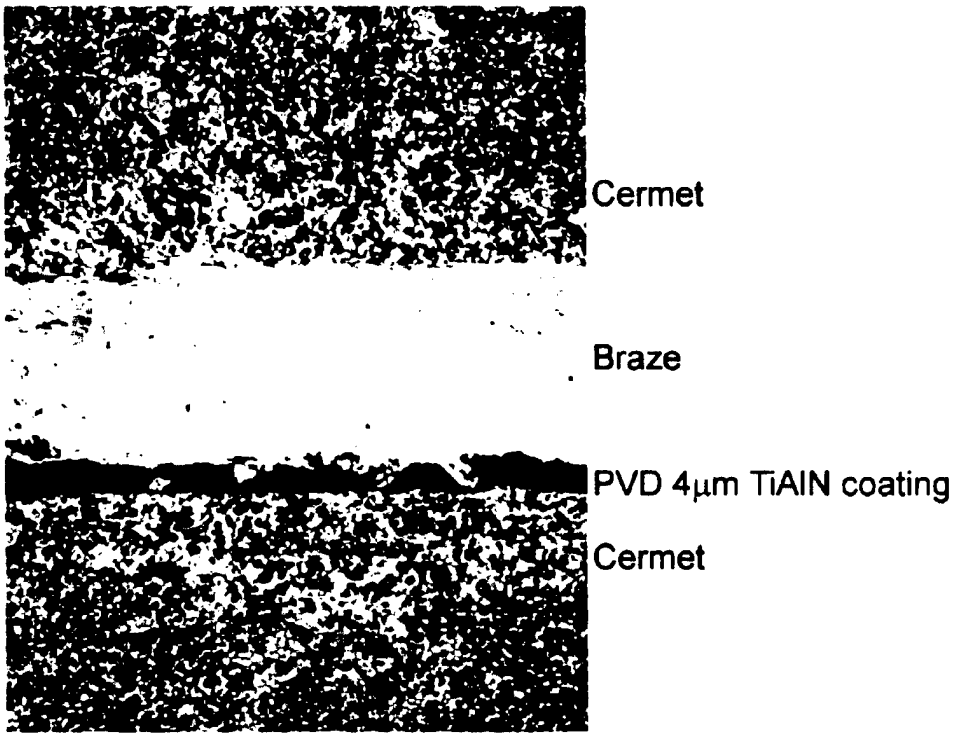

Fig.3

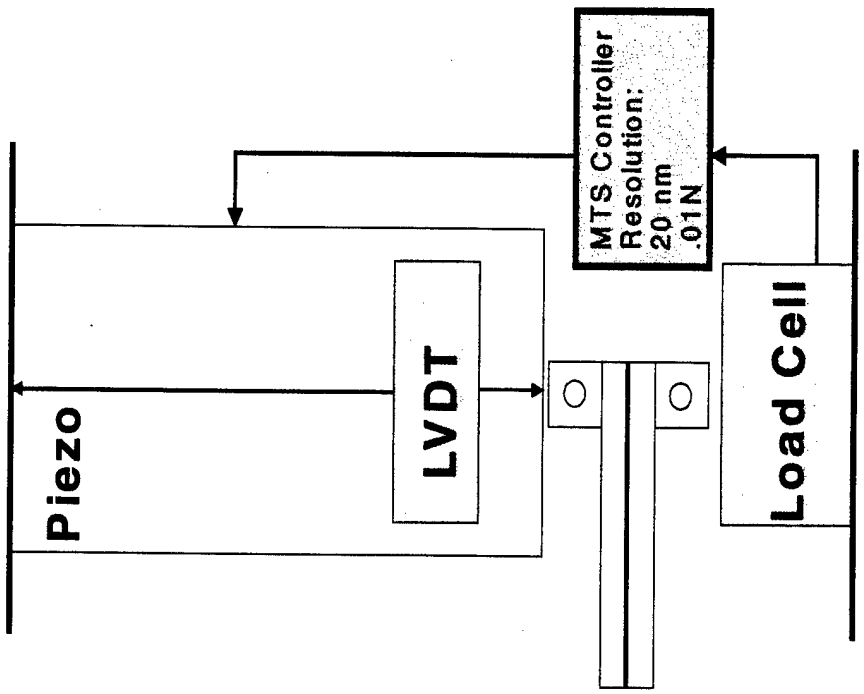

Fig.4

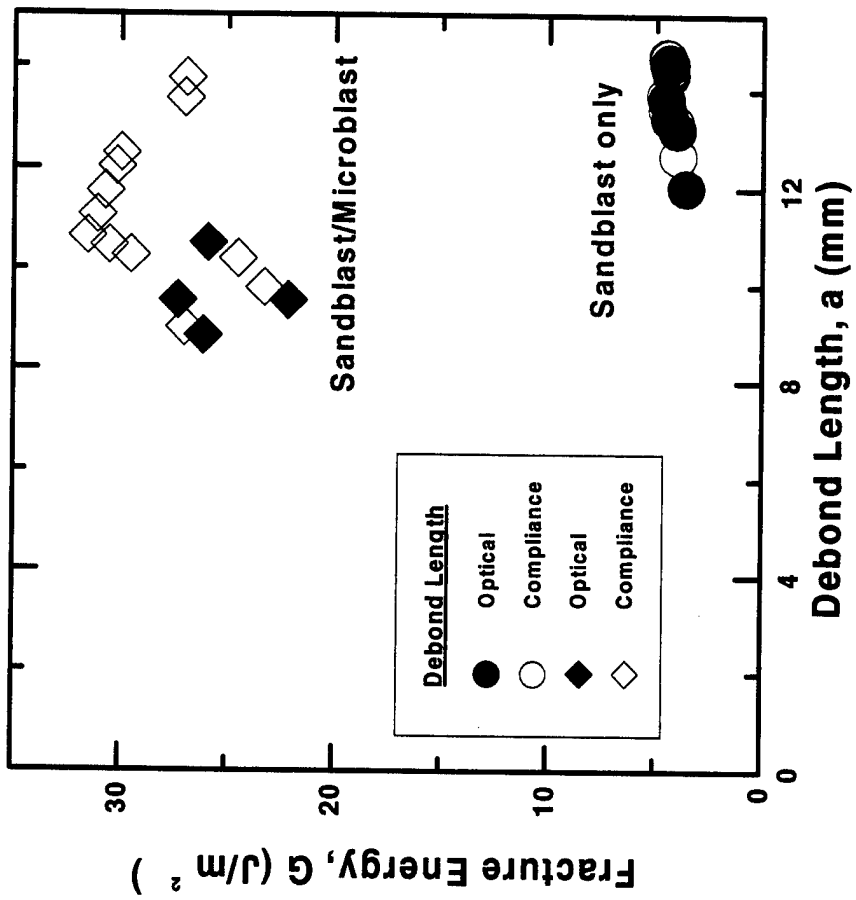
Fracture Energy, G (J/m²)
0
10
20
30
0
4
8
12
Debond Length, a (mm)
Sandblast/Microblast
Sandblast only
Debond Length
Optical
Compliance
Optical
Compliance

Fig.5

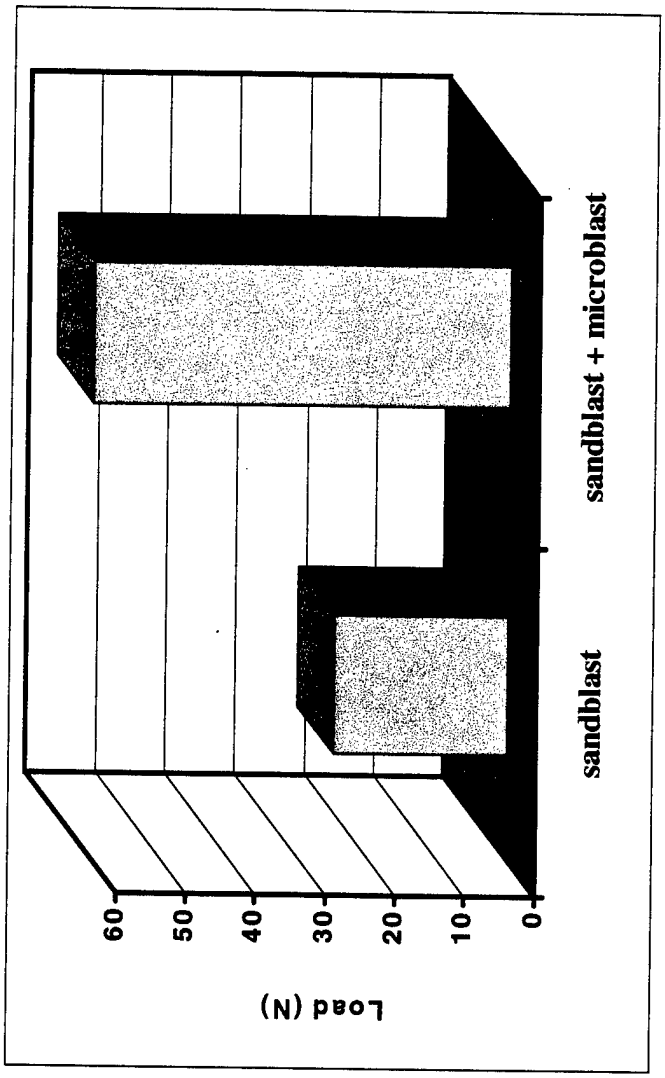

Fig.6

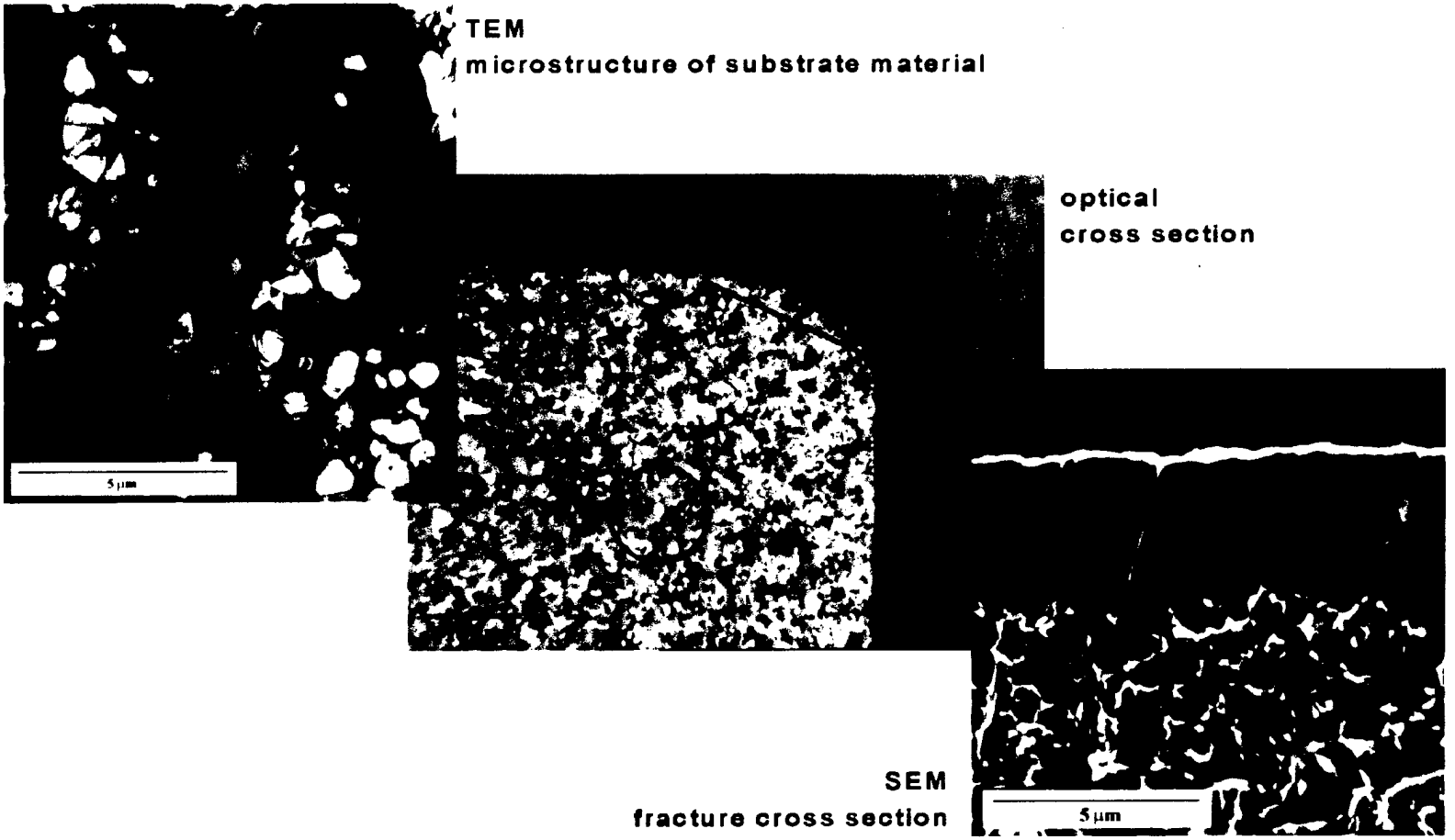
TEM
microstructure of substrate material
optical
cross section
SEM
fracture cross section
5 µm
5 µm

Fig.7

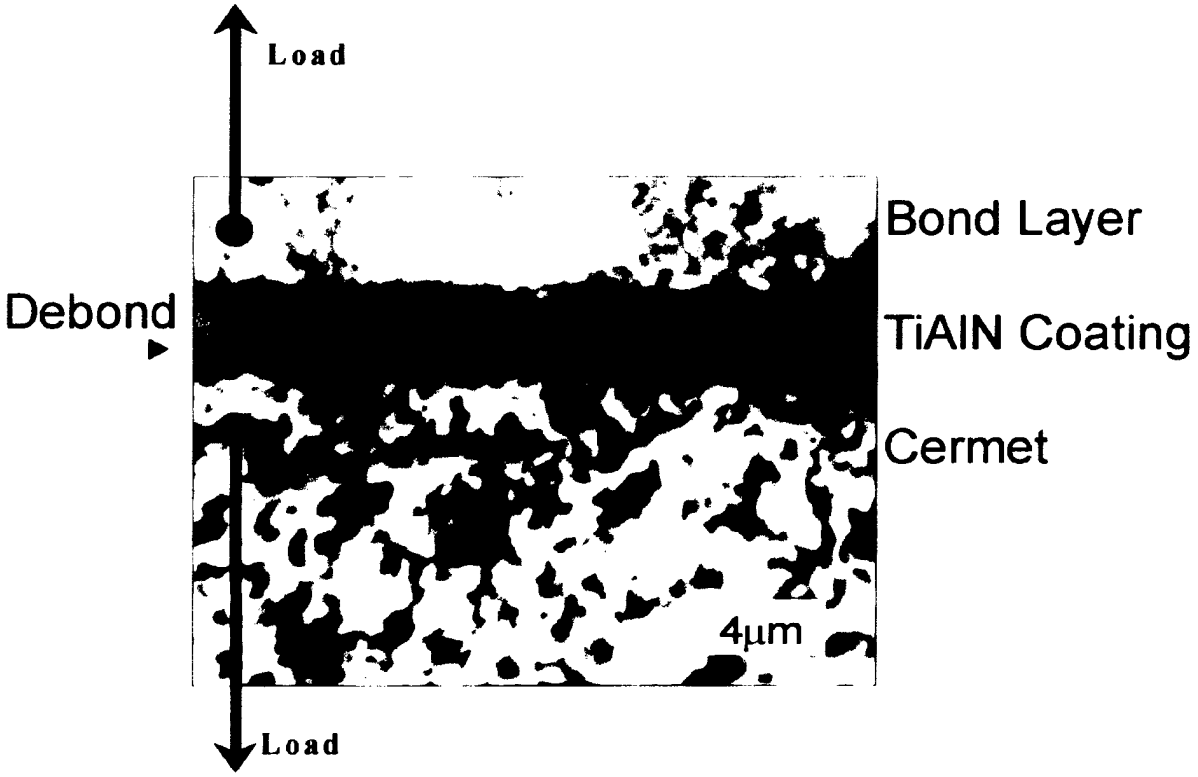

Fig.8

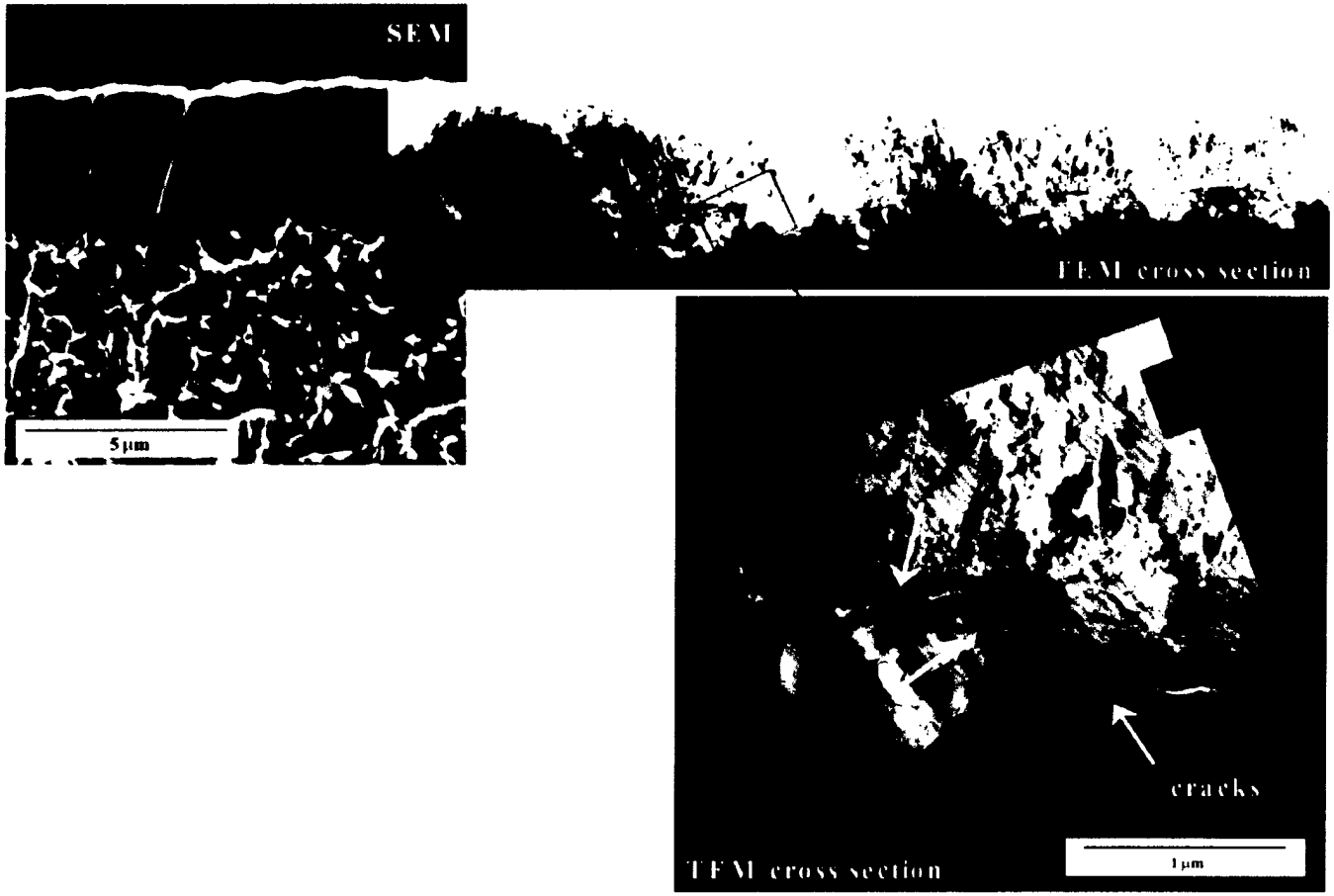

Fig. 9